Oct. 23, 1956 W. H. BENNETT 2,768,301

METHOD OF MASS SPECTRAL ANALYSIS WITH NEGATIVE IONS

Filed Aug. 8, 1951 3 Sheets-Sheet 1

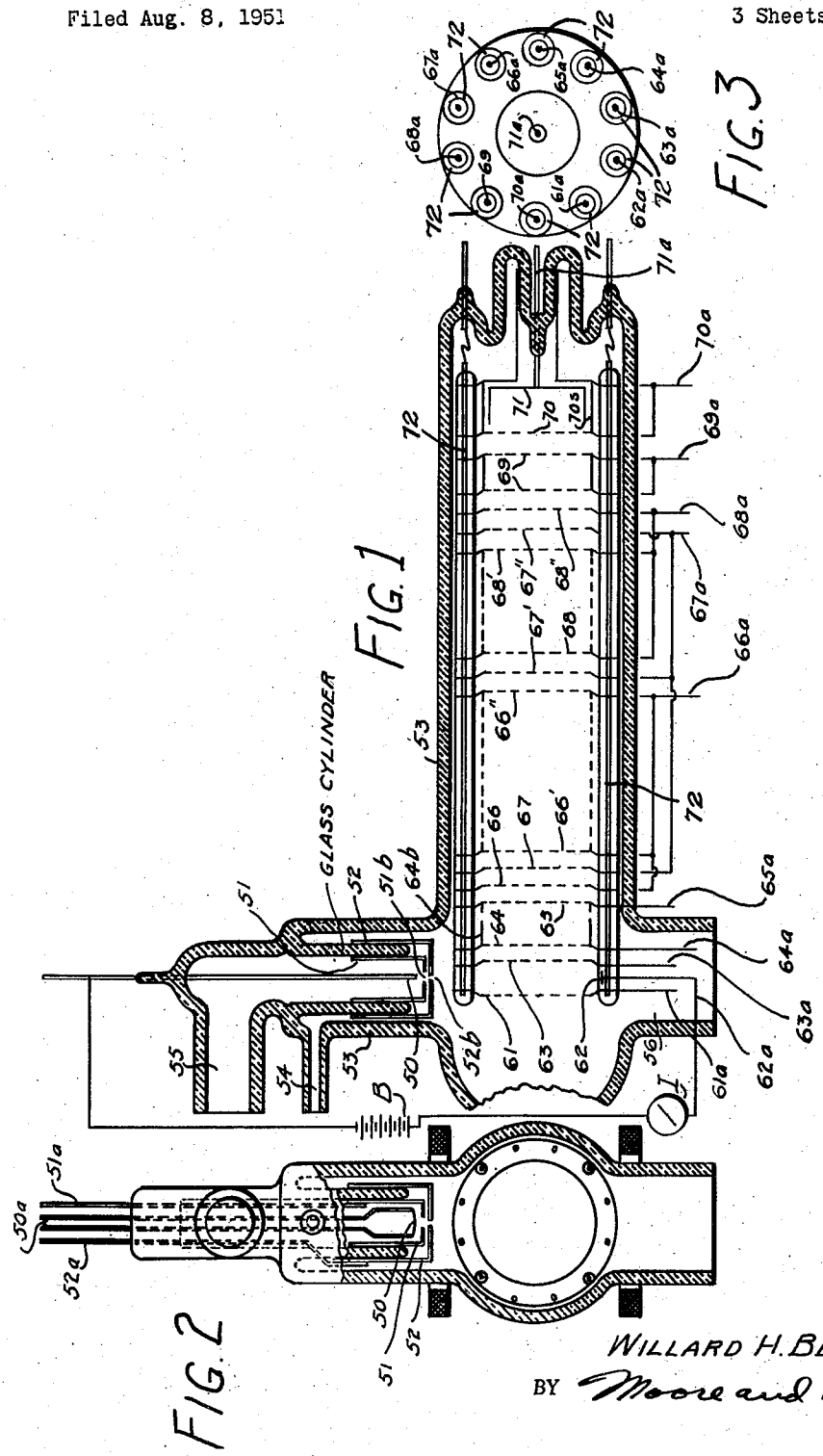


FIG. 1

FIG. 3

FIG. 2

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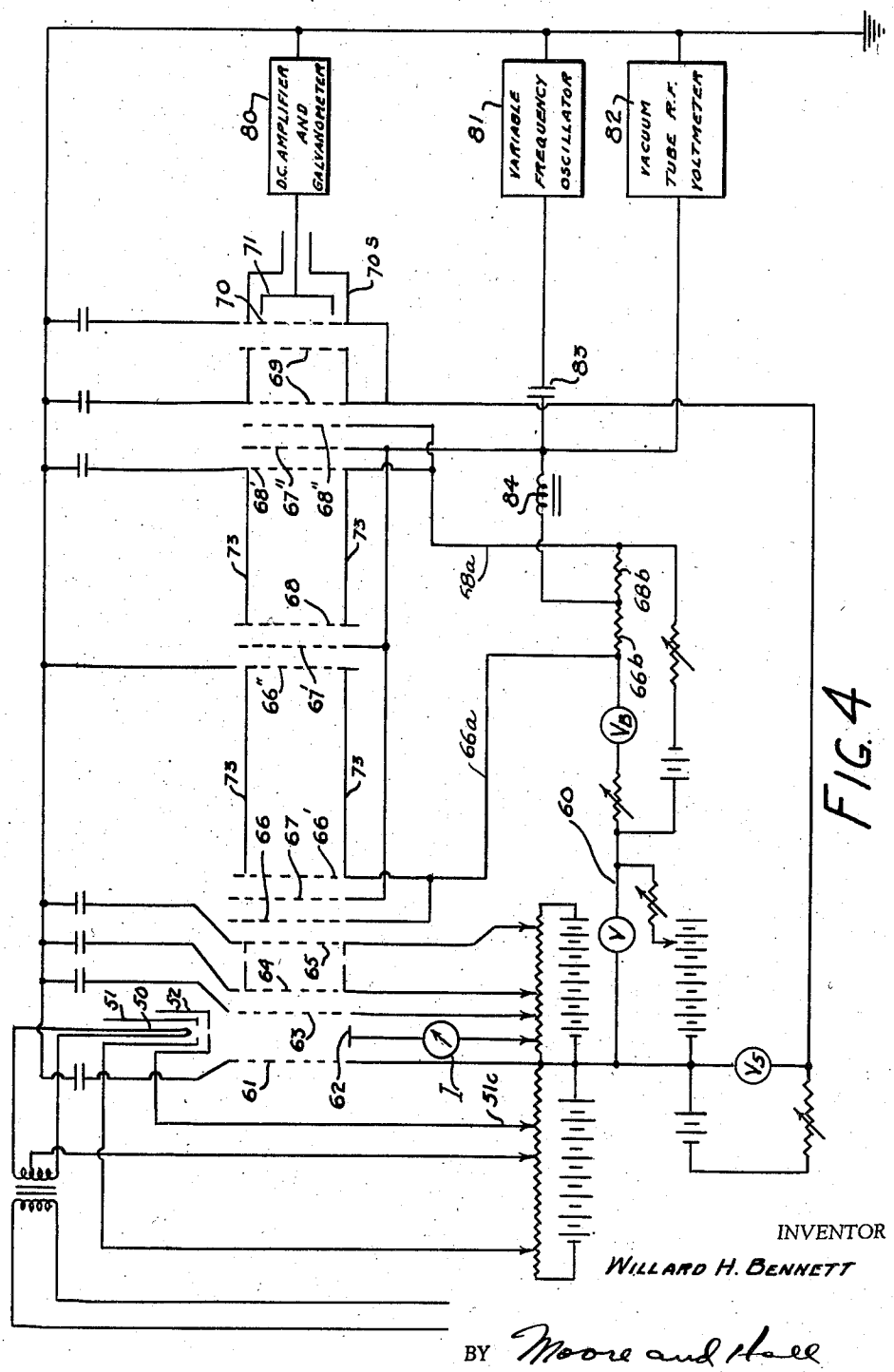


FIG. 4

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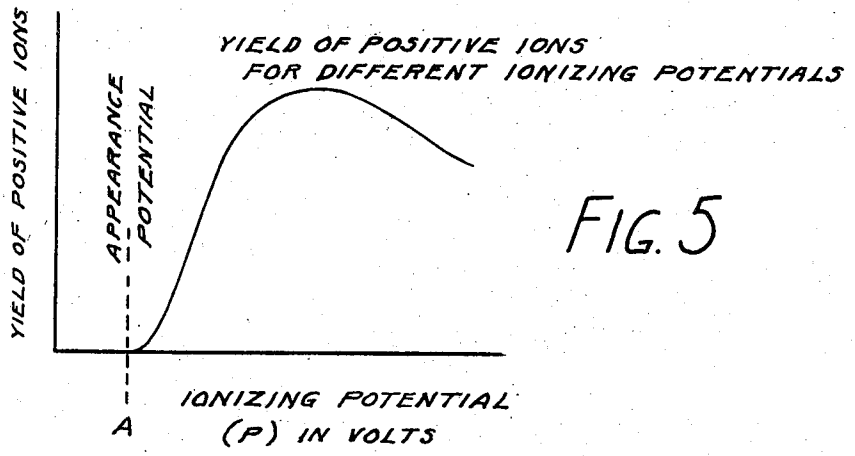


FIG. 5

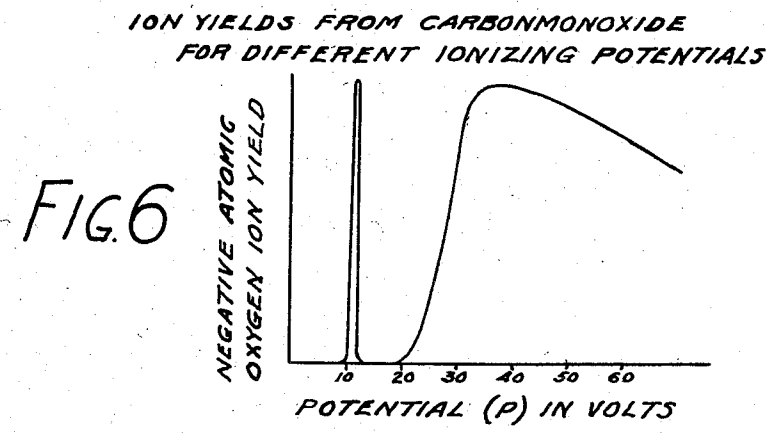


FIG. 6

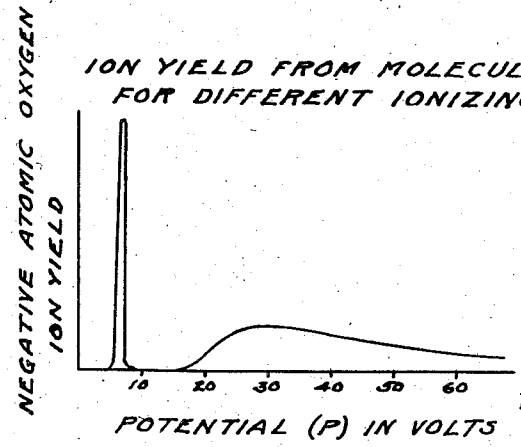


FIG. 7

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United States Patent Office 2,768,301 Patented Oct. 23, 1956

2,768,301

METHOD OF MASS SPECTRAL ANALYSIS WITH NEGATIVE IONS

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Application August 8, 1951, Serial No. 240,966

2 Claims. (Cl. 250—41.9)

This invention relates to methods of mass spectral analysis with negative ions.

An object of the invention is to provide a method of analysis whereby it is possible to distinguish between gases of the same molecular weight.

Other objects and further advantages will appear as this description proceeds.

Practically all, if not all, prior art successful mass spectral analysis has been with positive ions but I have discovered ways of rendering analysis with negative ions very useful in certain circumstances.

The invention is especially useful in cases where it is desired to analyze a mixture having two or more gases of the same molecular weight. Very often in such cases there is a critical bombardment velocity at which one of the two gases will produce negative ions and the others will not. Hence, by bombarding the mixture at this critical velocity and determining the number of negative ions produced, it is possible to conclude that a particular gas is present in the mixture in a particular amount. For example, to take a very simple case, it is impossible with prior art mass spectrometers to distinguish between carbon monoxide and molecular nitrogen because both have molecular weights of 28. Hence, it has been impossible to detect small percentages of carbon monoxide in the presence of air. However, carbon monoxide, if bombarded with 11 volt electrons, will yield negative oxygen ions whereas nitrogen will not yield negative ions if bombarded with electrons of any bombarding energy. Hence, the presence of small percentages of carbon monoxide may be determined by applying 11 volts accelerating potential to the electrons used in the ion source and then determining the masses of the negative ions produced. In that particular case, a complicating factor is that molecular oxygen also produces negative atomic ions, but such ions are produced only with electron velocities in the vicinity of 7 volts and none are produced with 11 volt electrons. Hence, by maintaining the potential of the ion source at the critical potential of 11 volts the desired determination may be made.

As another example of an application of my invention, assume that there is a mixture of three gases namely C_2H_4, CO and N_2, all of mass 28. By bombarding with 11 volt electrons producing negative oxygen ions it is then possible to determine the quantity of CO in the mixture by measuring the number of negative oxygen ions thereby produced. If the same analysis were attempted by prior art methods one would secure mass spectral lines for masses 1, 12, 13, 14, 15, 16, 24, 25, 26, 27 and 28 resulting in confusion and error.

While I am not limited to any particular apparatus so far as my process is concerned I have illustrated certain apparatus which I also illustrate and claim in my copending application S. N. 240,965, filed on even date herewith and entitled "Method of and Apparatus for Mass Spectral Analysis." The apparatus herein described is

an improvement on that disclosed in my published article entitled "Radio Frequency Mass Spectrometer," Journal of Applied Physics, vol. 21, No. 2, pages 143 to 149, February 1950 and is also an improvement on that disclosed in my prior copending application S. N. 196,024 filed November 16, 1950, entitled "Radio Frequency Mass Spectrometer."

In the drawings:

Figure 1 is a part cross-sectional and part schematic diagram of one form of tube that may be employed.

Figure 2 is a left hand end view of Figure 1.

Figure 3 is a right hand end view of the tube of Figure 1.

Figure 4 is a schematic diagram of a preferred hook-up of the invention.

Figure 5 is a curve illustrating the yield of positive ions of any typical gas for different ionizing potentials.

Figure 6 illustrates the negative ion yields of carbon monoxide for different ionizing potentials.

Figure 7 illustrates the negative ion yield of oxygen for different ionizing potentials.

Referring to Figures 1 and 2, the tube employs a cathode **50** which has leads **50***a*. A metallic cylindrical shield **51** has lead **51***a* for connecting the shield **51** to a variable potential approximately the same as that of the cathode. Shield **51** has an aperture **51***b* which is about four millimeters in diameter. Cylindrical metal electrode **52** has an aperture at its lower end of about two millimeters in diameter and coaxial with aperture **51***b*. These parts are all mounted in an envelope **53** which has an inlet opening **54** through which gases to be analyzed are admitted and it also has exhaust outlets **55** and **56** adapted to be connected to exhaust pumps for evacuating the tube. As is apparent, the exhaust outlet **55** primarily exhausts the interior of cylindrical cup electrodes **51** and **52** for the following purpose. The gas to be analyzed may have its chemical composition somewhat changed if it strikes the very hot cathode. Therefore, in order to make sure that none of such gas with changed composition passes into the main analyzing chamber, the tube is continuously exhausted at outlet **55** whereby any gases of changed composition are promptly removed from the envelope **53**. The gases to be analyzed are continuously fed into inlet **54** at a slow constant rate and are continuously exhausted by exhaust pumps connected to outlets **55** and **56**.

The potential on accelerating electrode 52 is highly positive relative to the cathode, say by thirty volts. As the electrons emerge through aperture **52***b* they pass between the two parallel grids **61** and **63**. The average potential of these grids relative to the cathode will be termed P, for simplicity. Assume that it is desired to effect a value of P of say eleven volts, which as has been said is the desirable potential used in detecting carbon monoxide. To carry out such an assumption the grid **61** would be made ten volts positive relative to cathode **50** and the grid **63** would be made twelve volts positive relative to the cathode **50**. As a consequence the electrons from cathods **50** form a narrow beam, known as a pencil of electrons, as they emerge from aperture **52***b* at a potential of thirty volts. They slow down to a speed of P volts as they enter the rigion between grids **61** and **63**. A magnet, or its equivalent in the form of suitable coils C, may be provided to produce a weak magnetic field which passes parallel to and in between the screens **61** and **63** and perpendicular to the electron stream emitted by the electron gun **50**—**52**. In this case the magnetic field may have approximately thirty gauss. The magnetic field could equally well be applied coaxial with the electron stream. In the latter case it may have a field intensity of approximately 100 gauss or more. When the field is perpendicular to the electron stream, as above stated, the potential difference between grids **61** and **63**

must be set at just a sufficient amount to give an electrostatic field between grids **61** and **63** whose force on electrons traversing this space just equals the force in the opposite direction on them due to the magnetic field. If P is the potential difference in volts between the cathode **50** and the midpotential between grids **61** and **63**, then the potential difference (in volts) between grids **61** and **63** should be equal to $0.0198\ H.d.\sqrt{P}$, where H equals the field gauss, and *d* equals the distance between grids **61** and **63**.

In order that it can be determined how many electrons are being produced, an item which it is often desirable to know in calibrating and using the tube, a small metallic electrode **62** is connected in series with a meter I, a battery B, and the cathode **50**.

In Figure 1 and 2 coils M are shown, as they may be conveniently used in lieu of the magnet above referred to.

In adjusting the apparatus for use, the magnet, or coils C as the case may be, is temporarily removed, the voltage on electrode **52** is adjusted to give maximum electron current, while the voltages on grids **61** and **63** are both set at the potential P (say eleven volts) initially in order to focus the beam. When the beam is in proper focus the magnet M is replaced and the potentials on grids **61** and **63** are rendered slightly different, according to the foregoing formula.

In view of the detailed disclosure in my published article, supra, and in my said prior copending application the theory of operation of the three stage mass spectrometer herein referred to need not be stated in detail. Adjacent grid **63**, there are grids **64** and **65** respectively connected to leads **64***a* and **65***a*, and these grids are charged positively at potentials intermediate those of grids **63** and **66**. The grid **64** tends to draw the negative ions through grid **63** and grid **65** tends to further accelerate the negative ions. Either or both of grids **64** and **65** may be omitted in which event the negative ions attracted into the mesh of screen **63** will then be attracted by grid **66**.

There are three groups of grids of three grids each, the grids of each group being closely spaced as compared to the spacing between groups. Grids **66**, **66′** and **66″** are connected to lead **66***a*. Grids **67**, **67′** and **67″** are connected to lead **67***a*. Grids **68**, **68′** and **68″** are connected to lead **68***a*. Leads **66***a* and **68***a* are connected to a source of positive polarity and lead **67***a* is fed with radio frequency potential. The distance between grids **67** and **67′** is preferably different than that between grids **67′** and **67″** and the two distances preferably are according to the ratio of 7 to 5.

The grids **69** may be used as repelling electrodes by applying a negative potential thereto. This potential is selected as described in said article and in said prior copending application, and is of value in repelling background electrons and ions leaving only ions that attained more than a predetermined velocity. However, grids **69** may be omitted if desired. Grid **70** is connected to cylindrical shield **70***s* and to lead **70***a* which in turn may be connected to lead **69***a*. The collector **71** is connected to a source of positive potential through its lead **71***a*, and it will attract negative ions that passed all of the other grids. Since collector **71** is made as positive as any other electrode in the tube, or preferably more so, it will repel any positive ions that have passed the grid **70**.

Figure 3 illustrates in more detail, the leads from the tube. The several grids are knitted wire screens mounted in washer-shaped disc holders, which holders are supported by horizontal rods **72**. Instead of bringing the leads vertically through the side wall of the envelope they pass horizontally through the rods **72** and out the right hand end of the envelope as shown in Figure 3. Cylindrical wire screens **73** connect grids **66′** and **66″** and grids **68** and **68′** inside of the tube. It should be noted that the uppermost horizontal rod **72** is not directly between cathode **50** and the space between grids **61** and **63**, hence there is nothing to prevent electrons from the cathode from passing to electrode **62**.

In Figure 4 a complete schematic diagram for operating the tube as a negative ion spectrometer. The amplifier and measuring instrument **80** is connected between the collector **71** and ground, and measures the flow of negative ions to the collector **71**. Variable frequency oscillator **81** provides the variable radio frequency potentials, and for many types of work a suitable frequency range may be from 100 kilocycles to 10 megacycles. The output of oscillator **81** is fed through condenser **83** and reactor **84**. The drop across reactor **84** is fed to the middle grids **67**, **67′** and **67″**, and also the leads **66***a* and **68***a* through resistors **66***b* and **68***b*. Vacuum tube voltmeter **82** measures the potential of the oscillator **81** whereby the latter may be adjusted and held constant.

In order to fully understand the theory of this invention it is desirable to review some basic facts. In Figure 5 there is illustrated the yield of positive ions for a typical gas as the ionizing potential P is increased. This curve assumes that a typical gas is admitted in to a typical mass spectrometer tube. The ionizing potential P, in the apparatus shown in Figure 1, is the average potential of grids **61**—**63**, relative to the cathode.

Figure 6 shows that in the case of carbon monoxide there are also negative ions produced at an appearance potential in a narrow range of ten to twelve volts and again in a broad range at voltages in excess of twenty volts.

Figure 7 shows the yield of negative ions when oxygen is the only gas in the tube. As shown there is no yield of negative ions for potentials between about eight and sixteen volts.

Nitrogen gas and inert gases will not yield negative ions when bombarded with electrons.

With the foregoing background information assume a mixture of gases that may contain nitrogen C_2H_4 and carbon monoxide. Further assume that it is desired to know if carbon monoxide is present, and if so, how much. First an analysis, may be made according to ordinary methods of mass spectrometry as contemplated in said article and in my said prior copending applications. This would give indications for mass lines numbers 1, 12, 13, 14, 15, 16, 24, 25, 26, 27 and 28. It could be concluded that there was present a mass of value 28 but it would be impossible to say what it was or how much of it was present.

According to the present invention the unknown mixture is fed into inlet **54** after the focus is suitably adjusted and the potential P set for about ten to twelve volts. If the bombardment produced negative ions for mass line 16 it would be obvious that carbon monoxide was present. By adjusting P to give the maximum intensity and measuring the number of such ions it is possible to conclude how much carbon monoxide is in the mixture. This would be done with the connections shown in Figure 4.

While I have illustrated my invention by showing how to detect carbon monoxide in the presence of nitrogen and ethylene, it is understood that the broader aspects of this invention are not limited to particular gases but cover the steps whenever applied to gases involving similar problems to those discussed herein.

To illustrate how the present method may be performed with other apparatus, I will describe now how the method may be practiced with the apparatus shown in Figures 1 and 2 of U. S. Patent No. 2,387,786 to H. W. Washburn, granted October 30, 1945, entitled "Analytical System." To practice my method, a change in the Washburn apparatus is required in that the polarity of electrodes **21** and **23** with respect to each other must be reversed. This may be done by reversing the polarity of the battery in the "ion beam deflection control circuit." The electrode **25** will then be highly positive. With this modified apparatus one would practice my method by fixing the potential between the cathode **17** and the drift space between

electrodes **21** and **23** at the critical value, which in the case of carbon monoxide is ten to twelve volts. A very sensitive recorder would be employed and would indicate the presence of negative oxygen ions and thus indicate the presence of carbon monoxide.

I claim to have invented:

1. The method of analyzing a gaseous mixture for the presence of a particular component thereof comprising the steps of bombarding the gaseous mixture with electrons of lowest energy range known to produce negative ions from the particular component, providing a segregating field of intensity required to segregate the negative ions from said particular component from ions of said other components of said gaseous mixture, and indicating the amount of said segregated ions present.

2. The method of analyzing a gaseous mixture for the presence of a particular component thereof, said component being characterized in that it will produce negative ions when bombarded with electrons within either of two ranges of velocities one of which ranges is a narrow range of velocities as compared to the other and the ionizing electron velocities of the narrow range are lower than those of the wider range, comprising the steps of bombarding the gaseous mixture with electrons whose velocities are within said narrow range, producing a

segregating field of intensity required to segregate the negative ions from said particular component from ions of other components of said gaseous mixture, and indicating the presence of said segregated ions.

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